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ScienceDirect

Procedia Engineering 87 (2014) 168 – 171

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2014, the XXVIII edition of the conference series

Twofold SiOx Films deposited by HFCVD: Its Optical, Compositional and Electrical Properties

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Abstract

Twofold non-stoichiometric silicon oxide (SiOx) films before and after of a thermal annealing are characterized by different techniques. The twofold SiOx films are obtained by hot filament chemical vapor deposition technique in the range of temperatures from 900°C to 1150°C. An important result is the optical energy band gap, which decreases as the growth temperature (Tg) increases from 2.15 to 1.8 eV. The absorption and emission properties are correlated with quantum effects in Si-nc and defects.The twofold SiOx films exhibit compositional changes with the variation of Tg and a restructuration (phase separation) take place with the thermal annealing.

Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: Silicon oxide; Photoluminescence; Transmittance; Current-Voltage; HFCVD.

1. Introduction

After discovery of visible light emission at room temperature in the porous silicon by Canham [1] in 1990, many investigators have studied emission properties of materials that contain Si nanoparticles (Si-nps) as the non-stoichiometric silicon oxide (SiOx), because of their technological importance and its interesting optoelectronic properties. In the SiOx films the absorption and emission properties are correlated with quantum effects in silicon nanoparticles, and also associated with defects [2]. From the technological standpoint, the average size of silicon nanoparticle (Si-np) offers band gap widths, which opens the possibility to tune the emission of light using nanostructured thin films in novel optoelectronic devices. Thermals annealing are generally used to enhance the

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Peer-review under responsibility of the scientific committee of Eurosensors 2014
doi:10.1016/j.proeng.2014.11.610

luminescent properties of the SiOx films. In this work, a study of the optical, compositional and electrical properties of twofold SiOx films obtained by hot filament chemical vapor deposition (HFCVD) technique, before and after of the thermal annealing is reported. Also the behavior of the material by varying the growth temperature, which opens the possibility for proposed novel optoelectronics applications in a future work.

2. Experiment

Simples SiO_x and twofold SiOx films were deposited on quartz and n-type silicon (100) substrates with 1 to 10 Ω-cm resistivity. These films were obtained by HFCVD technique in the range of temperatures from 900 to 1,150°C using quartz bars and porous silicon as the reactive solid sources. The deposition time was 5 min for the simples SiO_x films and of 10 min for the twofold SiOx films due to that the time for each layer was of 5 min. The relationship between the filament temperature (approximately 2,000°C) and the variation of the source-substrate distance (dss) of 4, 5 and 6 mm provides a change in the growth temperature (Tg) of 1,150°C, 1,020°C and 900°C, respectively. The twofold SiOx were made with two films deposited at two different temperatures, obtaining six possible combinations, 1,150°C/1,020°C, 1,150°C/900°C, 1,020°C/1,150°C, 1,020°C/900°C, 900°C/1,150°C and 900°C/1,020°C. The changes in the dss and Tg, consequently, modify the silicon excess and defects in the non-stoichiometric SiOx films. The thermal annealing was made using a nitrogen atmosphere at 1,100°C for one hour. Several spectroscopic characterization techniques were used. The film thickness was measured using a Dektak 150 profilometer. Room-temperature transmittance was measured using a UV-Vis-NIR Cary 5,000 system. FTIR spectroscopy measurements were done using a Bruker system. PL response was measured at room temperature using a Horiba JobinYvon spectrometer. Current-Voltage (I-V) curves were measured using a 4200-SCS Parameter Analyzer.

3. Results

Figure 1a) shows the UV-Vis transmittance spectra of the twofold SiOx films as-grown deposited on quartz. All the samples exhibited a relatively high transmittance (>70%) between 700 and 1000 nm. The change in the growth temperature produces a shift of the absorption edge towards lower wavelength related to a silicon excess change of the material [3]. Figure shows the absorption coefficient (α) of the twofold SiOx films as-grown obtained of the transmittance spectra and thickness (see table 1). The change in the growth temperature produces an increase of α tending to the silicon. The approximate values of the energy band gap (Eg) were obtained by the relationship known as Tauc plot [4] as shown inset Figure 1.The values of the Eg are shown in the table 1.

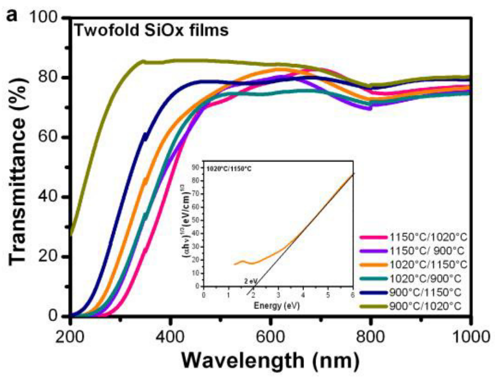

Fig. 1. Absorption coefficient as function of Tg and Eg

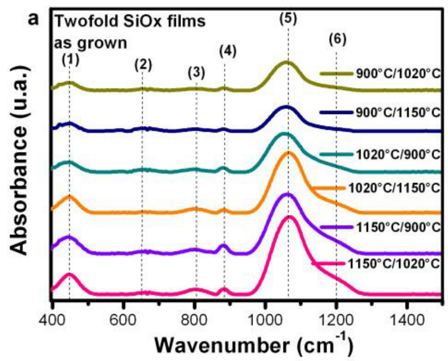

Fig. 2. FTIR spectra from Twofold SiOx films as-grown.

Table 1. Approximate values of thickness and energy optical band Gap.

Simples Samples	Temperature(°C)	Thickness (nm)	Energy Gap (eV)
S1	1150	470∓50	2.15
S2	1020	396 ∓60	1.8
S3	900	135 ∓35	2
Twofold Samples	Temperature(°C)	Thickness (nm)	Energy Gap (eV)
T1	1150/1020	734∓30	2
T2	1150/900	520∓13	2.25
T3	1020/1150	712∓12	2
T4	1020/900-	622∓20	1.8
T5	900/1150	225∓25	2.22
T6	900/1020	226∓21	2.18

Figure 2 shows the FTIR spectra from twofold SiOx films as-grown. The IR vibration bands are typical SiO_2 vibrations, (1) Si-O rocking, (3) Si-O bending,(5) Si-O stretching in phase, (6) Si-O stretching out of phase.(2) Si-H wagging and (4) Si-H bending are vibrations of hydrogen in twofold SiOx films as-growth, with annealing these peaks disappears and a separation of phase of Silicon nanocrystals (Si-nc) and SiO_2 is present in the twofold SRO films. Figure 3 shows the PL spectra from twofold SiOx films before and after of the thermal annealing, respectively. A wide PL spectrum with a similar shape to a Gaussian curve is observed for all the samples. For this reason the deconvolution was realized to PL spectra with which was obtained several peaks as shown the inset figure 3a), each of peaks represent the emission individually that are the components to the PL spectra. Therefore each peak has different origins. The PL spectra of twofold SiOx films as grown (see Figure 3a) illustrate a relatively weak PL intensity in the red with respect to PL intensity after a further annealing (see Figure 3b) main in the red. Figure 4 show IV curves of simples and twofold SiOx films.

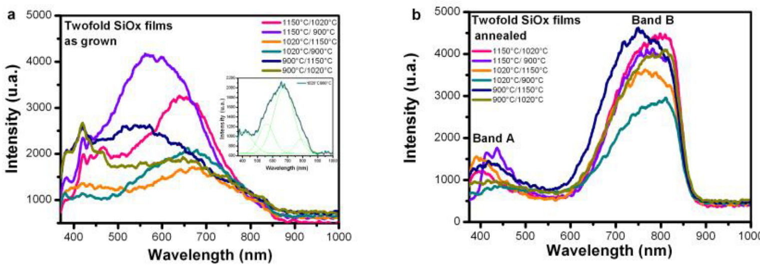

Fig. 3.(a) PL spectra from Twofold SiOx films as-grown (b) and annealed.

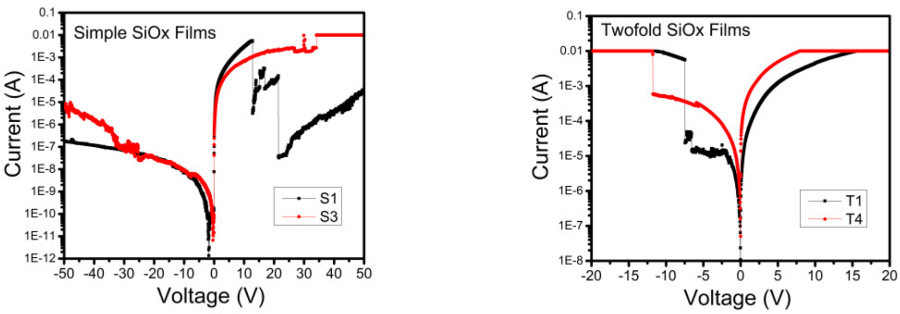

Fig. 4. Current-Voltage (I-V) curves of Simples and Twofold SiOx films.

4. Discussion

The optical band gap decreases nonlinearly when Si concentration continually increases [2]. Therefore, we may assume that the Si excess increases as the growth temperature increases as showed the table 1. The FTIR spectra show that before thermal annealing, the peaks found show a shift to lower wavenumber with decreasing of the growth temperature (Tg), indicating the change in the silicon excess. After thermal annealing, these shifts disappear and the position of the vibration modes corresponding to SiO_2, thus indicating a phase separation. According to the results of the compositional and optical properties of the twofold SiOx films, we can correlate the evolution of the stoichiometry (obtained by FTIR) with the reduction of the Eg (obtained by Transmittance), where the oxygen content decreased along with the increased of the growth temperature and in turn with reduce of the Eg. So, we may assume that the Si excess increases as the growth temperature increases. On the other hand, the mechanism of light emission of the twofold SiOx films is related to some kinds of defects produced during the growth process, as shown FTIR spectra, such as, weak-oxygen bonds (WOB), neutral oxygen vacancy (NOV), non-bridging oxygen hole center (NBOHC), positively oxygen vacancy (E' center), interstitial oxygen molecules and peroxide radicals [5, 6, 7]. Some of these defects, such as NOV and NBOHC are the principal radiative recombination centers or the luminescence centers. It is observed that when the thermal annealing is applied to the samples, a restructuring occurs (as shows FTIR spectra), because the temperature causes a phase separation and growth of Si-nc's. The most interesting is that not only emit in the orange-near infrared range (band B) but also violet-blue range (band A) and the green-yellow band disappears. So the dominant radiative defects have changed from E'δ o NBOHC defects to Si-O species (i.e. WOB and NOV defects). With respect to the PL intensity of the band B, this is greatly enhanced after the thermal annealing. It is reasonable to consider that the two mechanisms are not contradictory, but run parallel in the samples. The I-V curves shown behavior anomalous of the characteristics typical IV, in this case is necessary an analysis to understand this behavior.

Conclusions

In this work, twofold SiOx films were obtained by HFCVD technique with different growth temperatures, their optical, compositional and electrical properties were studied before and after of the thermal annealing. vibrational bands related to Si–H was observed in twofold SiOx films before annealing (as show FTIR spectra), which disappeared after thermal annealing. The behavior of the change in intensity and shifted of the FTIR and PL spectra is ascribed to changes of phase in this material, associated with several defects and Si-nps. The I-V curves show anomalous behavior.

Acknowledgements

This work has been partially supported by CONACyT-154725, PROMEP and VIEP-BUAP-2014. The authors acknowledge INAOE and IFUAP laboratories for their help in the sample measurements.

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